

Mechanisms of Oxidative Degradation. I. Oxidation of Synthetic Rubbers Catalyzed by Metallic Ions*

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Synopsis

The oxidative stability of rubbers depends on the structure of the rubber and the impurities contaminating the rubber. It is known that the oxidation of natural rubber is accelerated by the presence of metallic impurities. Besides GR-S rubber and nitrile rubber, the effects of metallic impurities on the oxidation of new rubbers, especially those introduced after the discovery of Ziegler-Natta catalyst, have not been reported. In the first part of this paper, the theoretical background on the mechanisms of metal-catalyzed oxidation is given. Most of the early work was carried out for the oxidation of hydrocarbons in the liquid phase. The difficulties in applying the liquid-phase results to the oxidation of high polymers in the solid phase are mentioned. The new rubbers used for this study are polyisoprene, polybutadiene, *cis*-poly-1,3-butadiene, styrene-butadiene copolymer, butyl rubber, ethylene-propylene terpolymer (EPT), propylene oxide rubber, polyacrylic rubber, and butadiene-acrylonitrile rubber. The effects of stearic acid and various stearates on the oxidation of these rubbers are presented. The number of electrons transferred by the metal ion during redox reactions was found to be related to the effectiveness of the ion as a catalyst. Both the high and low oxidation states of the metal ion were shown to be active catalysts, supporting the accepted theory of metal catalysis through a hydroperoxide decomposition mechanism.

INTRODUCTION

The effect of copper on the aging of rubber was first studied by Miller in 1865.¹ In 1891, Thomson and Lewis² showed that solutions of any one of a number of metallic salts painted on the surface caused the destruction of the acid-cured rubber at 60°C. Salts of the four metals considered—iron, copper, mercury, and manganese—have all been used as catalysts of either oxidation or reduction in various media. Other studies on the catalyzed deterioration of rubber were reviewed by Davis and Blake³ in 1937.

Chovin⁴ in 1942 reported the effect of copper on the oxidation of rubber with his kinetic measurements. Villain⁵ then showed that most copper compounds possessed the same catalytic activity. Later, Chovin⁶ found the

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relative potency of other metallic salts on the oxidation of vulcanized rubber to be cobalt sulforicinoleate, manganese pelagonate, copper oleate, iron pelagonate, copper sulforicinoleate, and copper pelagonate.

In 1952, Rao, Winn, and Shelton⁷ first published the effect of metallic soaps on the stability of vulcanized GR-S rubber. Leyland and Stafford⁸ in 1959 reported the effect of metallic contaminants on natural rubber, SBR, and nitrile rubber. The stabilization aspect was studied by Leyland and Stafford,⁸ and Kuzminskii⁹ in Russia. Many other new rubbers available since the discovery of Ziegler-Natta polymerization catalyst have not been reported, especially related to the metal-catalyzed oxidation.

This paper will discuss effects of a number of metallic stearates and stearic acid on the autoxidation of various rubbers. Other forms of metallic ions, synergism of metallic ions, and stabilization against metal ion-catalyzed oxidation will be reported in a future paper.

THEORETICAL BACKGROUND

Mechanism of the Metal-Catalyzed Autoxidation in the Liquid Phase

The mechanism of the gas-phase metal-catalyzed oxidation has been well established. The catalytic activity of the metallic compound has been correlated with its conductivity.^{10,11} In general, the *p*-type conductors, such as cuprous oxide, are considered to be good catalysts, while the *n*-type conductors, such as zinc oxide, are poor catalysts.

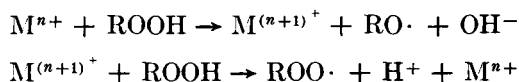
The oxidation of hydrocarbons in the liquid phase has been intensively reviewed.¹²⁻¹⁵ Generally the kinetic results are more reproducible for the liquid phase than for the solid phase due to the homogeneity of the medium. Therefore, the kinetic results obtained in the liquid phase have been frequently employed as guidelines for the study of the mechanism on the solid-phase oxidation.

The most important contribution to the understanding of the catalyzed oxidation in the liquid phase was made by Haber and Weiss¹⁶ in 1932 regarding the redox reaction of hydrogen peroxide catalyzed by the ferrous ion in the aqueous phase. This reaction was later reviewed by Uri.¹⁷ A similar redox reaction between phthalocyanines and olefins in the non-polar medium was reported by Cook¹⁸ in 1938. One year later, Ivanov, Savinova, and Mikhailova¹⁹ found that the heavy metal catalyst increased both the rate of formation and the rate of decomposition of the hydroperoxide during the oxidation of tetralin. The role of hydroperoxide was then fully established by Farmer and Sundralingam.²⁰

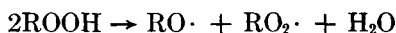
In 1946, Bolland and Gee²¹ published the well-known mechanism on the autoxidation of olefins. At the same time, George and Robertson²² described the mechanism of the catalyzed autoxidation of tetralin. The primary reaction is the chain formation of the hydroperoxide in which the catalyst both starts and stops the reaction chain. The subsequent reaction is the unimolecular decomposition of the hydroperoxide via a "heavy-metal

catalyst-hydroperoxide" complex to give the ketone. The hypothesis regarding the complex was further substantiated by Banks et al.²³

The equations proposed by Robertson and Waters²⁴ on the reaction between hydroperoxide and metallic ions have formed the basis for many later kinetic studies:



In the case of cobalt ion, the first of the above steps is a fast reaction, while the second is slow. The sum of these two steps gives the same products as in bimolecular thermal decomposition:



A significant kinetic study on the expansion of Bolland and Gee's scheme was made by Tobolsky et al.²⁵ The difference between the nonactivated and the activated schemes was postulated to be the rate of initiation. Most of their results, except the cobalt acetate-catalyzed autoxidation, were confirmed by Woodward and Mesrobian.²⁶ The detailed discussion on the accelerated autoxidation was reviewed by Bawn²⁷ and by Mesrobian and Tobolsky.²⁸

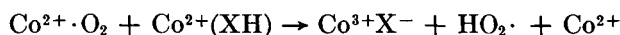
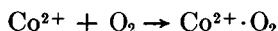
Roles of Metallic Ions in Autoxidation

The above-discussed kinetic schemes can be affected by the exact roles of metallic ions, which are not clearly understood. It has been shown that the metallic ions affect the rate of initiation and the rate of propagation. There are new findings to indicate that the metallic ions could affect the rate of termination if the metallic ions form complex with the R· radicals as reported by Kochi and Rust.²⁹

During the early stage of autoxidation, it has been suggested that the metallic ion might oxidize the hydrocarbon directly. However, the predominant reaction as discussed previously is the decomposition of hydroperoxide. Uri³⁰ suggested the three possibilities: (1) reduction activation of traces of hydroperoxide already present in the system; (2) direct reaction of a metal ion with oxygen:



and (3) complex formation of metal compounds with oxygen and subsequent formation of HO₂· radical:³¹



Whether the latter two of the above reactions will take place in the non-polar medium has not been demonstrated. In general, Uri hypothesized that there are always many trace metals present in the substrate, therefore the autoxidation in its initial stage is in fact a trace-metal-catalyzed reac-

tion. The form of the metallic compounds as well as the polarity of the medium could all affect the kinetics of the autoxidation.

Besides the above possibilities, Chakravarty³² also found an organo-metallic compound of lead with the structure, $R_3Pb \cdot RO_2$, during the autoxidation of oils. This could demonstrate the many concurrent roles of metallic ions during the autoxidation.

As in the case of the gas-phase oxidation of hydrocarbon, not all metals possess the same catalytic activities in a given medium. For instance, in the case of the oxidation of C_{15} - C_{25} straight-chain paraffins, the catalytic activities of the stearates were found by George et al.³³ to be $Fe > Co > Cu$. Wibaut and Strang³⁴ observed the catalytic activities for the oxidation of 2,5-dimethylhexane to be $Co^{2+} > Mn^{2+} > Ce^{4+} > Fe^{3+} > Cd^{2+} > Zn^{2+}$. A similar result on the oxidation of cyclohexene was obtained by Banks et al.:²³ $Co^{2+} > Mn^{2+} > Cu^{2+} > Fe^{3+}$. It should be noted that the last two series of catalytic activities are essentially identical to that of the metal-catalyzed decomposition of heptyl hydroperoxide in *n*-heptane at 80°C.:³⁵ $Co > Mn > Cu \gg Ni > Fe \geq Zn = \text{blank}$.

Mechanisms of the Metal-Catalyzed Oxidation of High Polymers

Many of the above-mentioned results regarding the liquid-phase oxidation have been applied to elucidate the oxidation mechanisms of high polymers in the solid phase. Several reviews on the oxidation of polymers³⁶⁻³⁸ and of elastomers³⁹⁻⁴¹ have discussed some aspects of the metal-catalyzed oxidation.

The major problem in the study of the kinetics of oxidation in the solid polymer is the diffusion phenomenon. Bauman and Maron⁴² demonstrated the effect of sample thickness upon the rate of oxidation of polybutadiene. The thicker the sample, the slower the rate. Their results showed that the diffusion of oxygen could interfere with the rate study and should be taken into account.

In the case of rubbers, the type of rubber, the state of vulcanization, and the presence of inhibitor could all affect the kinetics of the autoxidation.³⁹ Therefore, the presence of metallic catalyst for each case could deserve further separate studies. In this study, we investigate the effect of metallic ions on the oxidation of inhibited raw rubbers. Since the delicate kinetic study is not easy to achieve, we have used the absorption rate as defined in the experimental section to compare the effectiveness or the catalytic activities of various metallic ions. By using the absorption rate, we could eliminate the diffusion problem caused by the unequal thickness of the raw rubber films.

EXPERIMENTAL

Materials

All rubbers except Dow propylene oxide rubber were available commercially. The metallic impurities and the sources of rubbers are shown in

TABLE I
Metallic Impurities in Rubbers

Rubber	Al, %	Ca, %	Co, %	Cu, %	Fe, %	Li, %	Mg, %	Mn, %	Ni, %	Pb, %	Si, %	Sn, %	Ti, %	V, %	Zn, %
Polysoprene ^a	0.0002	0.0017	<0.0001	<0.0001	0.0005	0.0020	0.0006	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	—	—	0.0001
Polybutadiene ^b	0.0002	<0.0005	<0.0001	<0.0001	<0.0003	0.0024	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	—	0.0001
cis-Polybutadiene ^c	0.110	0.010	<0.0005	0.0005	0.0080	—	0.0080	<0.0001	<0.0005	<0.0010	0.0040	<0.0001	0.023	<0.0001	<0.0025
Styrene-butadiene ^d	0.0007	0.0046	<0.0001	0.0001	0.0018	0.058	0.0020	<0.0001	0.0001	<0.0001	0.0010	<0.0001	<0.0001	<0.0001	<0.0005
Butyl rubber ^e	0.052	0.018	<0.0005	0.0002	0.0050	—	0.0050	<0.0001	<0.0005	0.0010	0.0030	<0.0005	<0.0005	<0.0001	0.0070
Ethylene-propylene terpolymer ^f	0.0038	0.0018	<0.0002	0.0003	0.0020	—	0.0004	<0.0001	<0.0002	0.0010	0.0006	0.0001	<0.0001	0.0005	<0.0005
Propylene oxide rubber ^g	0.0010	0.0026	<0.0001	0.0001	0.0014	—	0.0001	<0.0001	<0.0005	<0.0010	0.0016	<0.0002	<0.0001	—	0.450
Polyacrylic rubber ^h	0.080	0.010	<0.0002	0.0001	0.0060	—	0.011	<0.0001	<0.0005	<0.0010	0.027	<0.0005	<0.0005	<0.0001	<0.0025
Nitrile rubber ⁱ	0.130	<0.0025	<0.0005	0.0002	0.0030	—	0.0045	<0.0001	<0.0005	<0.0012	<0.0030	<0.0005	<0.0005	—	<0.0025

^a Shell Isoprene rubber-309 (with antioxidant).

^b Firestone C.F. Diene (low antioxidant).

^c Phillips Cis-4 (with antioxidant).

^d Phillips Solprene X-40 (4/SK-4) (with antioxidant).

^e Polymer Corp. Polysar Butyl-101 (no antioxidant).

^f du Pont Nordel hydrocarbon rubber (with antioxidant).

^g Dow experimental (with antioxidant).

^h Goodyear Chemigum AC (RPA-1167A) (no antioxidant).

ⁱ U.S. Rubber Paracril BJLT \approx 32% acrylonitrile (with antioxidant).

TABLE II
Composition and Properties of Metal Stearates

Metal stearate	Valence	Major metal content, %		Free ^b fatty acid, % ^b	Softening points, °C. ^c	Remarks
		Determined ^a	Theoretical			
Cerium	4+	14.9	19.8	21.7	78-80	Specially prepared by Witco Chemical
Cobalt	2+	9.2	9.4	2.0	154	Witco
Copper	2+	10.5	10.2	3.9	110-115	Witco
Iron (Di)	3+	6.8	8.9	4.5	90-100	Witco
Lead	2+	21.7	26.7	0.1	102-104	Witco
Manganese	2+	9.3	8.9	—	110	Witco
Nickel	2+	10.9	9.4	5.2	135	Witco
Sodium	1+	7.5	7.5	—	200-210	Matheson, Coleman
Tin	2+	34.2	17.7 ^d	36.5	76	Specially prepared by Witco Chemical. (The result indicates it is a monostearate)
Zinc	2+	11.5	10.2	0.5	123-125	Witco

^a Our analytical results.

^b Free fatty acid was determined by titration.

^c Softening point was determined with a Fisher-Johns melting point apparatus by Witco Chemical as shown in their catalog.

^d Distearate.

Table I. Spectroscopic analysis was used to determine most of the impurities. Reproducibility of the trace metal analysis is $\pm 10\%$ of the amount reported. Lithium, aluminum, calcium, iron, magnesium, and zinc were commonly present in relatively large amount in the rubbers used for the study. Among them, iron is the only metal which could induce the catalyzed oxidation without any added metallic ions. In some cases the iron concentration was as high as 80 ppm.

The composition and properties of the metal stearates are listed in Table II. Most of the stearates were obtained from the Witco Chemical Company. It was expected that most of these stearates contained a small amount of transition metals. Furthermore, there was some fatty acid contamination with the stearates, especially tin and cerium stearates (Table II). These data are useful in helping interpret some boundary cases.

Equipment

Oxidation induction time and rates of oxygen absorption on the various rubbers were obtained using a modification of the Dornte procedure⁴³ for oxygen absorption.

Preparation of Sample

In order to prevent the raw rubber from degrading upon the heat treatment, a solution method was used to prepare the rubber-additive solution. All additives were put in at 0.1% weight concentration. The rubber was dissolved in either methylene chloride or carbon tetrachloride and thoroughly mixed. Aliquots, equivalent to 10.00 g. of polymer or rubber, were withdrawn and mixed with the additives which had previously been dissolved or dispersed in solvent. The solution or dispersion was then thoroughly agitated by tumbling for at least 1 hr. and cast in an aluminum dish (1.5-in. diameter) and allowed to evaporate for 1 hr. at room temperature. The stock solution was kept under nitrogen at all times.

The thickness of the film was between 20 and 30 mils (1–1.5 g. of rubber). For the same series of runs, it was impossible to prepare the same thickness, therefore, a thick sample was used to insure that the sample was only partially oxidized to a maximum thickness in the polymer.

Rate of Oxygen Absorption

The rate of oxygen absorption commonly used is expressed in milliliters of oxygen per gram of polymer per hour. As discussed previously, this rate has been shown by others to vary with the thickness of the polymer sample. It is known that for the kinetic study a very thin film can be used to eliminate the error caused by the thickness. However, this is not easy in the case of raw rubber. An alternative method was used for this study. The rate of oxygen absorption, expressed in milliliters of oxygen per hour, was found to be reproducible. The effect of thickness on both kinds of rate is shown in Figure 1. For a thick film, the rate in milliliters

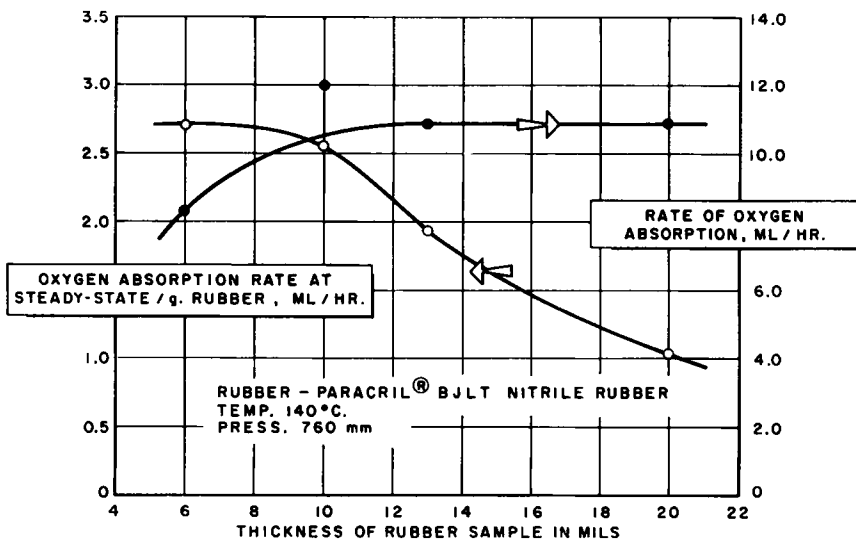


Fig. 1. Effect of sample thickness on absorption rates.

per hour is constant due to the limit of the oxygen diffusion. For our purpose where the relative efficiency of catalyst was concerned, we found that the rate in milliliters per hour was the appropriate measure to use. Just as with other oxygen-uptake measurements, a certain reservation is needed to justify the precision of the measure.

It should be pointed out that the important effect of the metallic catalyst is to shorten the induction time. Within the experimental error, the induction time is independent of the weight and the thickness of the sample. The amount of catalyst, however, can affect the induction time. Since the induction time is another measure of the relative efficiency of the catalyst, it is not feasible to study the uninhibited oxidation except for those rubbers which are stable to oxidation at elevated temperatures.

RESULTS AND DISCUSSION

The oxygen-absorption measurements for various rubbers were carried out at different temperatures because the oxidizability of rubbers varies with the structure of rubber and with the content of inhibitor. The induction time is shown in Table III, and the rate of oxygen absorption is given in Table IV. The relative activities of various catalysts are discussed below according to the type of rubber.

Polyisoprene

The structure of Shell synthetic *cis*-polyisoprene is essentially identical to the structure of the natural rubber. The main difference is the contaminations in the natural rubber, such as, the resin acids. Therefore, the effect of metallic ions on both rubbers should be very similar. The strongest

TABLE III. Induction Time for the Metal-Catalyzed Autoxidation of Rubbers^a

Rubber	Tem- perature, °C.	Blank	Stearic acid	Induction time, min.										
				Stearates										
				Ce	Co	Cu	Fe	Pb	Mn	Ni	Na	Sn	Zn	
Isoprene rubber (Shell)	110	66	61	—	17	38	48	—	9	67	69	—	64	
Diene rubber (Firestone)	120	240	120	138	66	72	84	90	66	192	192	372	180	
Cis-4 polybutadiene (Phillips)	150	100	142	39	20	39	19	100	53	149	98	88	152	
Solprene X-40 SBR (Phillips)	120	174	90	186	72	90	72	216	60	186	132	96	234	
Polysar Butyl-101 (Polymer Corp.)	130	78	42	36	66	84	48	66	72	60	84	198	66	
Nordel EPT	150	284	206	85	22	32	24	237	65	205	355	223	185	
Propylene oxide rubber (Dow)	120	107	41	48	22	48	81	65	66	54	67	52	78	
Polyacrylic rubber (Goodyear)	130	84	84	54	84	30	30	54	96	72	90	54	90	
Nitrile Paraeril BJLT (U.S. Rubber)	120	138	114	132	120	528	72	114	108	108	126	—	126	

^a All additives at 0.1 wt.-% concentration.

TABLE IV
Rates of Oxygen Absorption by Rubbers at Steady State^a

Rubber	Tem- perature, °C.	Oxygen absorption, ml./hr.											
		Blank	Stearic acid	Ce	Co	Cu	Fe	Pb	Mn	Ni	Na	Sn	Zn
Isoprene rubber (Shell) Diene	110	23.0	30.0	—	72.0	36.0	31.0	—	46.0	31.0	34.0	—	35.0
rubber (Firestone)	120	32.8	24.6	30.5	61.5	48.0	51.8	41.5	43.5	34.1	32.0	6.3	37.5
Cis-4 polybutadiene (Phillips)	150	39.5	22.5	62.0	43.5	35.6	97.0	51.0	38.0	24.0	39.6	45.0	23.8
Solprene X-40 SBR (Phillips)	120	35.0	17.0	55.5	125.0	54.0	31.0	39.3	42.0	43.0	35.0	21.1	39.4
Polysar Butyl-101 (Polymer Corp.)	130	5.9	6.8	6.0	7.7	6.2	5.1	4.6	5.2	5.3	6.6	4.1	5.0
Nordel EPT (du Pont)	150	38.0	30.0	32.0	62.0	46.0	60.0	28.0	33.0	34.0	34.0	25.5	23.0
Propylene oxide rubber (Dow)	120	36.2	35.8	34.5	49.8	28.0	33.0	36.4	50.4	37.1	31.7	36.1	38.6
Polyacrylic rubber (Goodyear)	130	4.9	6.3	7.1	5.5	8.4	7.8	6.0	5.7	5.8	6.2	6.0	6.1
Nitrile Paracril BJLT (U.S. Rubber)	120	6.4	12.0	15.0	22.0	10.0	29.0	13.0	12.0	9.0	12.0	—	11.0

^a All additives at 0.1 wt.-% concentration.

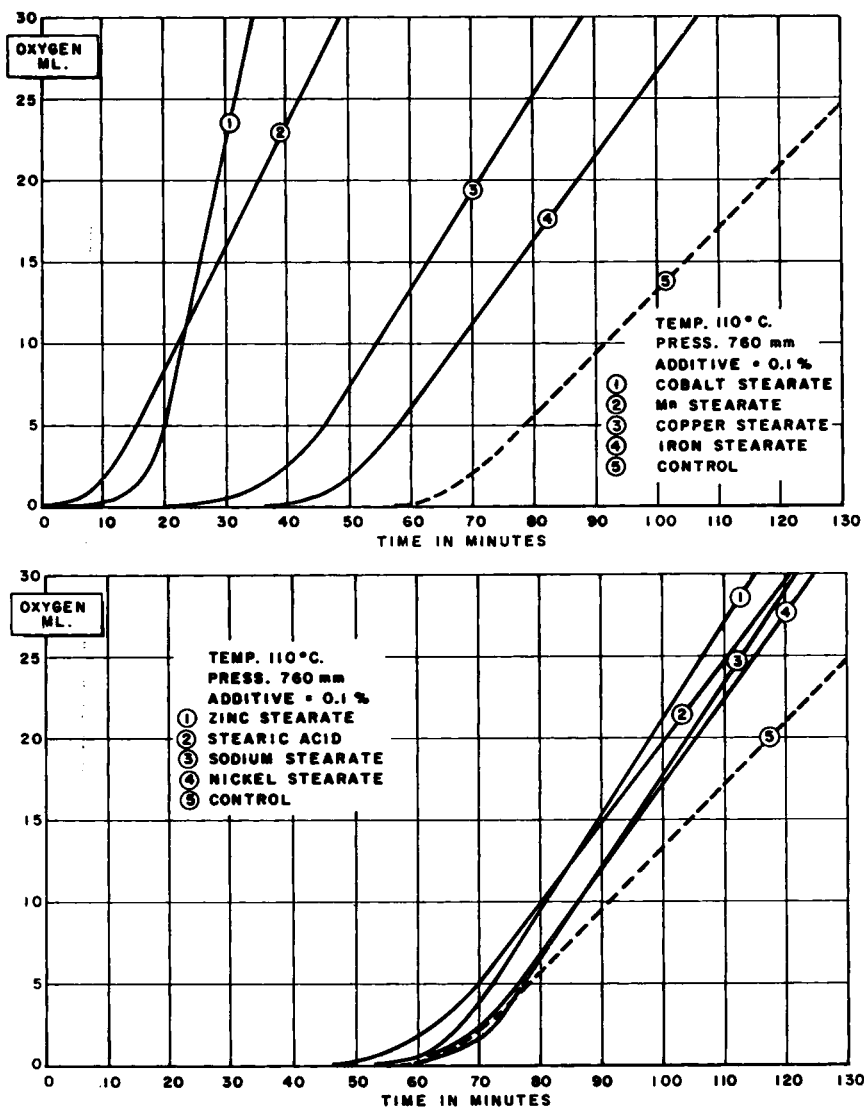


Fig. 2. Oxygen absorption by polyisoprene rubber (Shell Isoprene rubber, type 309).

catalysts were cobalt and manganese. According to the induction time, the activities were $\text{Mn}^{2+} \geq \text{Co}^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+}$ (Fig. 2a). According to the rates, the activities were $\text{Co}^{2+} > \text{Mn}^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+}$. The rates were in accord with Chovin's result on natural rubber.⁶ Stearic acid, zinc, sodium, and nickel stearates (Fig. 2b) showed weak catalytic activities.

Polybutadiene Rubber

Firestone Diene rubber is a linear polybutadiene rubber polymerized with butyllithium. Diene rubber contains approximately 7.5% 1,2 vinyl

isomer and 32–35% *cis* isomer. This rubber is characterized by its narrow molecular weight distribution, nonstereoregularity, amorphous nature, and high purity. In general, according to the induction time, Co^{2+} and Mn^{2+} ions were the strongest. The reactivities could be arranged as follows: $\text{Co}^{2+} = \text{Mn}^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+} > \text{Pb}^{2+} > \text{Ce}^{4+}$. The rates followed a slightly different order: $\text{Co}^{2+} > \text{Fe}^{3+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Pb}^{2+} > \text{Ce}^{4+}$. It should be noted that stearic acid had a medium catalytic activity. Whether stearic acid tends to activate the originally contaminated impurities, such as iron, is not fully understood. Other ions, such as zinc, nickel, and sodium, exerted some weak activities. Stannous stearate unexpectedly appeared to be an inhibitor. It may be worthwhile to point out that the apparent activity of cerium could be weakened by the presence of a large amount of fatty acid in the sample. (Table II.)

cis-Poly-1,3-butadiene

Phillips Cis-4 rubber contains only a small amount, if any, of other isomers of polybutadiene. The effect of metallic ions in this instance is specific to the hydroperoxide formed at the α carbon. Otherwise, the activities of metallic ions should follow the general pattern. The results show that iron was somewhat unusually strong for Cis-4 polybutadiene. The reactivities according to the induction time were $\text{Fe}^{3+} \geq \text{Co}^{2+} > \text{Ce}^{4+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Mn}^{2+}$. The rates were $\text{Fe}^{3+} > \text{Ce}^{4+} > \text{Pb}^{2+} > \text{Sn}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+} > \text{Cu}^{2+}$. Other unusual results were the weak antioxidant activities of stearic acid, zinc, and nickel stearates.

Styrene-Butadiene Rubber

Phillips Solprene X-40 rubber, resembling GR-S structurally, is polymerized in solution by a stereospecific catalyst. The incorporation of 25% styrene renders the rubber somewhat more stable than polybutadiene alone. The previously discussed strong catalysts showed only medium activities, to judge from the degree of the reduction of the induction time of the blank. Under a separate study, polystyrene alone was found to be stable in the presence of these catalysts at elevated temperatures as high as 190°C. It may be deduced that the action of the metallic catalyst is predominantly restricted to the butadiene portion at the temperature, 120°C., of the oxygen absorption.

The reactivities from the induction time alone followed the order $\text{Mn}^{2+} \simeq \text{Co}^{2+} = \text{Fe}^{3+} > \text{Cu}^{2+} > \text{Sn}^{2+}$ (and stearic acid). However, the difference in rate was large enough to justify the cobaltous ion to be the most reactive catalyst. Nickel, lead, and zinc stearates appeared to be unreactive based on the rates and very weak antioxidants according to the induction time. In general, the results agree with those obtained by Rao, Winn, and Shelton⁷ on the emulsion-polymerized SBR.

Butyl Rubber

Polysar Butyl 101 is a copolymer of isobutylene and isoprene. The rubber contains 0.65 mole-% of unsaturation and no antioxidant. The predominant site for the oxygen attack would be at the α carbon of the isoprene unit, which is only a fraction of the total copolymer. Based on the induction time, cerium, iron, and stearic acid appeared to be more reactive than others. This polymer did not follow the general pattern. The difference in the rates (5–8 ml./hr.) was also very small, making it difficult to determine which metal was the most reactive. Cobaltous ion may be more reactive than the others if the difference is significant. Of the other metallic salts, stannous stearate acted like an antioxidant.

Ethylene-Propylene Terpolymer (EPT)

Du Pont Nordel hydrocarbon rubber contains a third diene monomer with an internal double bond. Both the diene and the propylene units are subject to the oxygen attack.

Based on the induction time, the relative reactivities of the metallic ions decrease in the order: $\text{Co}^{2+} = \text{Fe}^{3+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Ce}^{4+}$. This is in accord with the relative rates. Other metallic ions except sodium showed very weak reactivity. Surprisingly, sodium stearate appeared to be a weak antioxidant. Under a separate study, the catalytic activities of metallic ions on the oxidation of polypropylene were shown to be nearly identical to the above results for the EPT rubber. The reactivities were in the order: $\text{Co}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Pb}^{2+} > \text{Fe}^{3+} > \text{Ce}^{4+}$.

Propylene Oxide Rubber (POR)

This rubber is a Dow experimental product which is a copolymer of propylene oxide and an allylic ether. The presence of the ether oxygen linkage besides the α hydrogen causes some additional oxidation problem. In the metal-catalyzed oxidation, it appeared that nearly all metallic ions possess strong to medium relative reactivities. Among them, cobaltous ion showed the highest reactivity. Strangely, stearic acid appeared to be the next strong catalyst. The order of reactivities was: $\text{Co}^{2+} > \text{Ce}^{4+} > \text{Cu}^{2+} > \text{Sn}^{2+} = \text{Ni}^{2+} > \text{Pb}^{2+} = \text{Mn}^{2+} > \text{Zn}^{2+} = \text{Fe}^{3+}$.

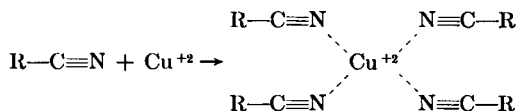
Polyacrylic Rubber

Goodyear Chemigum AC is another new rubber with a polar functional group. It is a 95/5 ethyl acrylate copolymer intended for high-temperature ($>275^\circ\text{F}$.) oil-resistant application. This rubber did not contain antioxidant, as shown by the short induction time. Basically, the oxidation can take place at the carbon containing the tertiary hydrogen. The reactivities as shown by the induction time were $\text{Cu}^{2+} = \text{Fe}^{3+} > \text{Ce}^{4+} = \text{Pb}^{2+} = \text{Sn}^{2+}$. The rates were too small to permit differentiation of the reactivities of these ions. However, both copper and iron caused higher rates of oxygen absorption. The low reactivities of cobaltous and man-

ganous ions for the oxidation of this rubber are difficult to explain. It was noted that zinc and sodium stearates and stearic acid appeared not to be catalysts.

Butadiene-Acrylonitrile Rubber

U.S. Rubber Paracril BJLT butadiene-acrylonitrile rubber contains approximately 32% acrylonitrile. In essence, this rubber can also be classified as a polar rubber and is intended for oil-resistant applications. The presence of the nitrile group appeared to reduce the catalytic activities of the metallic ions as indicated by the small change in induction time. Among them, iron was the strongest catalyst. The reactivities followed the order $\text{Fe}^{3+} \gg \text{Mn}^{2+} = \text{Ni}^{2+} > \text{Pb}^{2+} > \text{Co}^{2+}$, according to the induction time, but cobaltous ion was second to ferric ion according to the relative rates. The most unusual result was that the cupric ion acted as an antioxidant. This result has been confirmed after a recently obtained BJLT nitrile rubber was used for the similar evaluation. In order to explain this result, it is postulated that the cupric ions could form a coordination compound with the nitrile group:



However, we do not yet have an explanation for the antioxidant ability of the proposed chelate.

SUMMARY AND CONCLUSIONS

The metal-catalyzed autoxidation of rubbers was studied by oxygen absorption measurements. The effects of metallic stearates and stearic acid on the oxidation of polyisoprene, polybutadiene rubber, *cis*-poly-1,3-butadiene, styrene-butadiene rubber, butyl rubber, ethylene-propylene terpolymer (EPT), propylene oxide rubber, polyacrylic rubber, and butadiene-acrylonitrile rubber were discussed. In general, the oxidation is similar to that in liquid phase: (1) those metals with one-electron transfer during the redox reaction, such as cobalt, copper, manganese, cerium and iron, are more reactive; (2) those metals with two-electron transfer, such as lead and tin, are less active; (3) those metals with no electron transfer, such as zinc and sodium, are normally not reactive.

Many exceptions have been found throughout this study. The deviation from the generalization could be caused by the unusual structure of the rubber, such as the nitrile rubber, or by the interaction between the metallic ions and the antioxidants contained in the rubbers. However by using an excessive amount of metallic salt (0.1%), this type of interaction, if any, should not interfere with the observed increase in the induction time or in the absorption rate.

Since most metals follow the general pattern of the redox reaction and the reactivities of metallic ions follow the same sequence in the decomposition of hydroperoxide,³⁵ it appears that the reaction involving a hydroperoxide is unquestionable. Whether the hydroperoxide exists in a free state or in a complex^{22,23} with the metallic ions needs further study. The facts that the rubbers with labile C—H bonds oxidize more readily and that both the high and the low oxidation states of the metal ions²⁴ can initiate the catalyzed reactions support the generally accepted theories regarding the metal-catalyzed oxidation through a hydroperoxide intermediate. Possibly there are other roles of metallic ions³⁰ which could take place in the solid phase; this study, however, has not revealed such roles besides several unexpected results of metals acting as antioxidants. It should also be mentioned that the effect of metallic ions on pyrolysis was not studied and might be different from what was discussed in this paper.

The results obtained during this study imply the importance of the type and the amount of metallic impurities in the new synthetic rubbers which are mostly prepared by the use of metallic catalysts. These metallic impurities can cause an accelerated rate of oxidation and thus result in poor physical properties and undesirable color of the end product.

Note: The oxygen absorption-time curves for all the rubbers tested may be obtained from the senior author.

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Résumé

La stabilisation des caoutchoucs dépend de la structure du caoutchouc et des impuretés que le contaminant. Il est connu que l'oxydation naturelle du caoutchouc est accélérée par la présence d'impuretés métalliques. A côté du caoutchoucs GR-S et du caoutchouc nitrile les effets d'impuretés métalliques sur l'oxydation des caoutchoucs nouveaux en particulier ceux introduits après la découverte de Ziegler-Natta n'ont pas encore été rapportés. Dans la première partie de ce travail, on rappelle le fondement théorique des mécanismes d'oxydation catalysée par les métaux. La plus grande partie du travail antérieur a été effectuée sur l'oxydation d'hydrocarbures en phase liquide. Ces difficultés d'appliquer les résultats en phase liquide à l'oxydation des hauts polymères à l'état solide sont mentionnées. Des nouveaux caoutchoucs utilisés pour cette étude sont le polyisoprène, le polybutadiène, le poly-1,3-*cis*-butadiène, le copolymère styrène-butadiène, le caoutchouc butylique, les polymères éthylène-propylène (EPT), le caoutchouc d'oxyde de propylène, le caoutchouc polyacrylique et le caoutchouc butadiène-acrylonitrile. Les effets de l'acide stéarique et des différents stéarates sur l'oxydation

de ces caoutchoucs sont présentés. Le nombre des électrons transférés par l'ion métallique au cours des réactions rédox est lié à l'efficacité de cet ion comme catalyseur. A la fois, les états d'oxydation supérieur et inférieur de l'ion métallique sont les catalyseurs actifs, ce qui supporte la théorie acceptée de la catalyse métallique par un mécanisme de décomposition par hydroperoxyde.

Zusammenfassung

Die Oxydationsbeständigkeit von Kautschuk hängt von der Struktur des Kautschuks und von den im Kautschuk enthaltenen Verunreinigungen ab. Es ist bekannt, dass die Oxydation von Naturkautschuk durch die Gegenwart metallischer Verunreinigungen beschleunigt wird. Ausser bei GR-S-Kautschuk und Nitrilkautschuk, wurde noch nicht über den Einfluss metallischer Verunreinigungen auf die Oxydation neu entwickelter Kautschuke, besonders der nach der Entdeckung der Ziegler-Nattakatalysatoren eingeführten, berichtet. Im ersten Teil der vorliegenden Mitteilung wird der theoretische Hintergrund für den Mechanismus der metall-katalysierten Oxydation entwickelt. Die meisten früheren Arbeiten befassten sich mit der Oxydation von Kohlenwasserstoffen in flüssiger Phase. Die Schwierigkeiten bei der Anwendung der Ergebnisse in flüssiger Phase auf die Oxydation Hochpolymerer in fester Phase werden erwähnt. Folgende neu entwickelte Kautschuke wurden untersucht: Polyisopren, Polybutadien, *cis*-Polybutadien-1,3- Styrol-Butadiencopolymers, Butylkautschuk, Äthylen-Propylenterpolymeres, Propylenoxydkautschuk, Polyacrylkautschuk und Butadien-Acrylnitrilkautschuk. Der Einfluss von Stearinsäure und verschiedenen Stearaten auf die Oxydation dieser Kautschuke wird gezeigt. Die Anzahl der durch das Metallion bei Redoxreaktionen übertragenen Elektronen stand in Beziehung zur Wirksamkeit des Ions als Katalysator. Sowohl die oxydierte als auch die reduzierte Form des Metallions erwiesen sich als aktive Katalysatoren; damit gewinnt die bekannte Theorie des Hydroperoxydzersetzungsmechanismus der Metallkatalyse eine Stütze.

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